Surface and Colloid Chemistry of Clays

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A. Crystal Structure and Charge Distribution

Clay minerals are composed of small plate-like particles ranging in diameter from a few hundredths of a micron to several microns.[1,2] Making up each such platelet are one or more unit layers, stacked like a deck of cards; the crystal structure of the unit layers consists of sheets of tetrahedrally coordinated silica in combination with sheets of octahedral alumina or magnesia.

Three-layer clays such as montmorillonoids[2a] and illites have a unit layer consisting of a sheet of octahedral alumina or magnesia sandwiched between two sheets of tetrahedral silica.[3,4] A schematic representation of the crystal structure of the prototype silica-alumina mineral, pyrophyllite, is shown in Figure 1; an example of a clay mineral with similar structure is montmorillonite. This structure is termed dioctahedral, as only two out of every three octahedral sites are occupied. In contrast, illites and the montmorillonoids vermiculite and hectorite (and the synthetic hectorite-type clay, Laponite) are trioctahedral; the central sheet of the unit layer is predominantly magnesia, and ideally all octahedral sites are occupied. The prototype trioctahedral mineral is mica. The exposed basal faces of these three-layer clays consist of siloxane, that is Si-O-Si.

In a two-layer clay, such as kaolin, the unit layer is composed of one sheet of silica and a sheet of alumina;[3,4] the basal faces of these clays are thus half siloxane and half hydroxylated alumina.

Electrokinetic studies of clay sols indicate that, at all pH values above two or three, clay particles carry a net negative charge which is compensated by the presence of positive counterions. The origins of this charge on the clay lattice are believed to be isomorphic substitution, lattice imperfections, broken bonds at the edges of the particles, and exposed structural hydroxyls.

van Olphen[3a] suggests that the principal source of the observed negative charge on the clay particles is isomorphic substitution. The latter implies that the constituent metal ions of the lattice are replaced isomorphically by cations of lower charge. For relatively highly charged clays (*e.g.*, montmorillonite, vermiculite) chemical analyses reveal sufficient substitution (approximately 80-100 mequiv/100 g of clay) to account for most of the observed cation exchange capacity.[3b,4] In montmorillonite, most of the substitution is in the central alumina sheet; in vermiculite, large amounts of substitution also occur in the silica sheet, with up to 25% of the silicon being replaced by aluminum.[1] In a clay with a low cation exchange capacity (such as kaolinite), isomorphic substitution does occur, although the small amount of substitution which would account for the negative charge on the lattice (1-10 mequiv/100 g of clay) is difficult to measure accurately.[3c,4] Hence, it appears likely that isomorphic substitution is the chief source of negative charge in highly charged clays, and there is some evidence to indicate that it contributes to the negative charge on clays with low cation exchange capacities.

The absence of a constituent metal atom from its place in the clay crystal sructure would result in a negative charge on the lattice. Such imperfections are difficult to measure, as the very small amount of material that need be missing to contribute significantly to the particle charge is analytically negligible compared to the total weight of the same metal in the clay. Other types of lattice imperfections which may contribute to the negative charge (*e.g.*, dislocations, localized bond breakages) are also difficult to detect analytically.

It has been suggested that the broken bonds at the edges of the particles may be in part responsible for the negative charge on the lattice. However, there is strong evidence to indicate that the edges of clay particles are positively charged in the neutral and acid pH ranges.[3d,5-19] Electron micrographs of a mixture of kaolinite and a negative gold sol[3d] show the negative gold particles to be adsorbed along the edges of the kaolinite platelets. These positive charges are believed to arise from reactions of the type

$$\text{-Al-O-Al-} \longrightarrow (\text{-Al-O}^- + \text{-Al}^+) \xrightarrow{H_2O,\,H^+} 2\ \text{-Al-OH}_2^{\ +}$$

A number of studies indicate that the edges of clay particles are positively charged at pH <7-8,[14-17] although some data suggest that the edges are neutralized already at pH ~ 6.[18,19]

The presence of oppositely charged faces and edges on clay particles leads to considerable edge-to-face flocculation in aqueous suspension. Such floc structure is broken down by addition of base[13,20,21] or of various anions.[8,21-24] Schofield and Samson[21] have shown that kaolinite can also be deflocculated by small, negative montmorillonite particles (presumably by their adsorption

TABLE I. Specific Surface Areas of Kaolinite and Montmorillonite by Various Methods

	Kaolinite		Montmorillonite	
Method	Surface area[a]	Ref[b]	Surface area[a]	Ref[b]
BET (N_2)	11.0–38.4	26–31, 129, 175, 181	27–71	26, 28–32, 65, 129
BET (H_2O)	29.9–33.4		400–440	28, 65
BET (O_2)	10.6–24.4	27		
BET (Kr)	10.0–24.5	27		
BET (NH_3)			90.7–121.3	26
BET (ethyl chloride)	14.6–29.9	181		
BET (air)	8.4–23.7	27		
Methylene blue	15.2–26.6	27		
Air permeability	1.7–2.9	27		
Ethylene glycol			725	31
Negative adsorption (Cl^-)	16	31	85–750	22, 31, 33, 34, 46
Theoretical calculations	1071	29	700–800	28, 29, 32, 202

[a] In m^2/g. [b] References are numbered as they appear in the text.

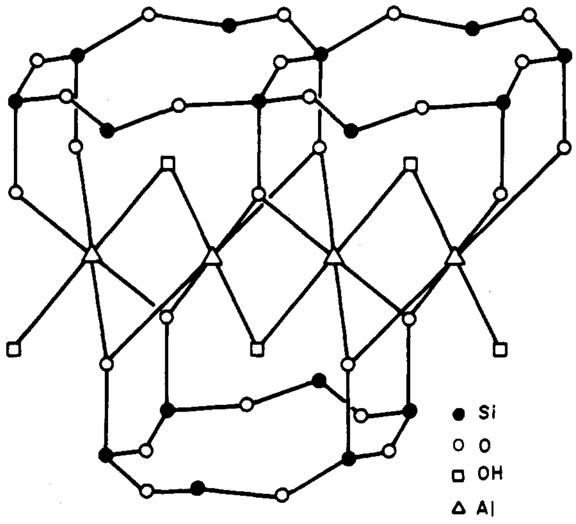


Figure 1. Crystal structure of prototype of three-layer silica-alumina clay (schematic).

onto the positive edges of the larger kaolinite platelets). Hence, the case is strong in favor of positive, rather than negative, edges on clay particles in neutral and acidic media.

The dissociation of structural hydroxyl groups is another possible source of negative charge. However, such hydroxyls are bound to aluminum or magnesium atoms (Figure 1) and might more reasonably be expected to protonate.[25]

The negative charge on the clay particles is compensated by adsorption of cations. In clays which swell in the presence of water the counterions are held on the external surfaces of the aggregates and between the unit layers, whereas in nonswelling clays the counterions are sorbed onto the external surfaces only. In aqueous suspension, some of these cations may remain in a closely held Stern layer; others diffuse away from the surface and form a diffuse double layer. Provided that they are not fixed (*i.e.*, irreversibly adsorbed) by engaging in strong, specific bonding with the clay or by being trapped between unit layers that have collapsed together irreversibly (lattice collapse), the counterions can undergo ion exchange with other cations present in the system. The magnitude of the cation exchange capacity of a clay depends largely on the type of clay and to a lesser extent on the source of a particular sample. An extensive study by the American Petroleum Institute[1] reports cation exchange capacities of various montmorillonites as 85–160 mequiv/100 g of clay, whereas the exchange capacities of the kaolinite samples ranged from 1.5 to 20.2 mequiv/100 g (with most of the values between 3 and 10 mequiv/100 g); there was no significant difference between North American and European clays of the same type.

The experimentally measured specific surface area of a clay mineral depends on the type of clay and the method of measurement employed; among clays of the same type the values vary from sample to sample, and in any one mineral sample the nature of the counterions present may influence the measured surface area. Examples of specific surface areas of different samples of kaolinite and montmorillonite, determined by various methods, are given in Table I. The theoretical surface areas were calculated from the weights of the unit cells, and their dimensions as indicated by X-ray diffraction.

For a given sample of kaolinite the BET nitrogen surface areas are largely independent of the counterion on the clay.[26] BET adsorption isotherms of nitrogen, oxygen, krypton, and air gave similar values for the surface area of a given kaolinite sample;[27] from other work, it also appears that water vapor, ethyl chloride, methylene blue, and negative adsorption yield comparable data. Surface areas of kaolinite samples measured by air permeability[27] are only one-tenth of those measured by adsorption methods; the latter, in turn, give surface area values equal to only a few per cent of the theoretical value of 1071 m^2/g.

Montmorillonite typically yields larger experimental specific surface areas than kaolinite.[26,28-31] In the case of montmorillonite with alkali metal counterions, the BET nitrogen surface areas become slightly larger as the unhydrated radius of the cation increases.[28,32] In the case of water vapor and ammonia adsorption it was difficult to see any trends in the measured surface area with varying counterions.[26,28] Negative adsorption data gave values varying from near theoretical for natural montmorillonite[31] to 560 and 85 m^2/g for sodium and calcium montmorillonite, respectively;[22] surface areas measured in this manner decrease with increasing charge or increasing unhydrated radius of the counterion.[33,34] Surface areas from ethylene glycol adsorption data are approximately equal to the total theoretical area of montmorillonite.[21]

B. The Electrical Double Layer

The application of the diffuse double layer theory to describe the ionic distribution in the vicinity of clay particles has met with mixed success. As a rule, experimental results can be quantitatively interpreted by the theory only if certain empirical corrections are made.

Eriksson[35] calculated the distributions of sodium and calcium counterions competing at the clay–water interface and concluded that diffuse double layer theory can satisfactorily account for the physical situation. However, Bolt[36,37] and Ottewill[38] found it necessary to assume the adsorption of counterions in the Stern layer in order to interpret their results. This was supported by Weiss, *et al.*,[39] who noted that the extent of the diffuse double layer at the clay–solution interface depended upon the affinity of the cation for the clay.

Shainberg and coworkers[40-44] have applied the diffuse double layer theory to ionic distributions at the montmorillonite–water interface. They found that the theory is in relatively good agreement with the experimental data when the surfaces of the particles are sufficiently separated to permit formation of complete diffuse layers. However, if the proximity of adjacent surfaces restricts diffuse layer formation, as is the case at the internal surfaces of aggregates stacked face-to-face, the theory is no longer satisfactory and must be modified. By taking into consideration such factors as Stern layer adsorption, ionic size, and hydration of ions and of the clay surface, they were able to more reasonably describe the physical situation at the clay–solution interface. Edwards, *et al.*,[45] have found that better agreement between the theory and experiment may be achieved if the surface charge is considered to be discrete rather than smeared and uniform; in this manner, ion-pairing could be included in the calculations.

The surface areas of montmorillonite calculated from chloride exclusion measurements according to the double layer theory were lower than those determined by other means; furthermore, the area from the exclusion data decreased with increasing affinity of the positive counterion for the clay surface.[22,33,34,46] The authors suggest that the failure of the theory in this instance could be caused by such factors as partial blocking of negative surfaces by adjacent particles, incomplete double layer formation on some or all surfaces, and ion-pair formation between the counterions and negative sites on the clay, which would lower the effective negative charge. If allowance is made for partial dehydration of the cation, sufficient ion-pair formation would occur to account for most of the discrepancy between the theory and the experiments on negative adsorption. In addition, it is possible that positive adsorption of chloride ions on the edges of the clay particles can account for some of the deviation observed.

Bolt and coworkers[5,47] found that the double layer theory was reasonably satisfactory in explaining the positive and negative adsorption of anions (except at low concentration) for montmorillonite but not for vermiculite.

A parallel-plate model has frequently been employed to describe the interactions between face-to-face oriented unit layers in clay minerals (*cf.* Ottewill, ref 38), especially with respect to their behavior in the presence of water. At low separations, the clay platelets exhibit greater resistance to reduction of the interlayer distance than predicted. Numerous authors[38,48-53] have attributed this to hydration effects; bound, and probably structured, water of hydration must be driven out of the interlayer region before the unit layers may be brought closer together. On the other hand, under some circumstances, the resistance to increasing the interlayer spacing is greater than predicted by theory.[48,49,53] van Olphen[3,48,49] suggests that a small proportion of the clay platelets hold the unit layers of face-to-face aggregates together by adsorbing on the edges of the stacks of unit layers. This is substantiated by the fact that neutralization of the positive edge charge by adsorption of phosphate ions produces systems more in agreement with double layer calculations.[54] Furthermore, the nature of the counterions in the interlayer can affect the entire situation. Interlayer separations in sodium-saturated montmorillonite and vermiculite could be explained by the diffuse double layer theory with moderate success in some[55-57] but not all[51,58,59] cases. The distance between unit layers in calcium montmorillonite is too small for the formation of a complete diffuse double layer, and, therefore, the theory cannot be applied in its simple form.[55,58,60]

Geuze and Rebull[61] showed that the double layer theory qualitatively explains edge-to-face flocculation, although the agreement with the experiments may be somewhat fortuitous considering the relative simplicity of their model. Recently, the coagulation and peptization of montmorillonite-type clays was treated in terms of the DLVO theory by using the platelet model and assuming an asymmetrical charge distribution.[62,63]

For a detailed examination of double layer treatment of colloidal clays, reference may be made to Ottewill's extensive review of the subject.[38]

C. Particle Association in Suspension

Particle association in clay suspensions can occur *via* face-to-face, edge-to-face, and edge-to-edge interactions. A variety of structures are possible, depending upon the mode of interparticle bonding. Face-to-face association can produce stacks whose major dimensions are similar to those of unassociated unit layers, the chief difference being in the thickness of the resultant platelet. If only partial overlap of faces occurs, extended ribbons or lamellae may be formed whose major dimensions are much different from those of the original particles. If the clay platelets are joined edge-to-face, a "card-house" structure is formed, resulting in voluminous flocs and eventually, at high solids concentrations, in gels. Edge-to-edge association can produce ribbons, lamellae, or card-house flocs. Methods used to study the mode and strength of interparticle bonding include X-ray diffraction (ref 32, 48, 51, 64–69), optical measurements (optical density, birefringence, and light scattering) (ref 21, 69–81), swelling pressure (ref 51, 53, 56, 57, 82), electron microscopy (ref 1, 55, 83, 84), rheology (ref 6, 13, 16, 21, 79, 80, 85–88), and porosity (ref 89, 90).

The amount of face-to-face aggregation in a clay and the interlayer spacing depend on a number of factors. Some clays, such as kaolinite, exist as stacks of unit layers under all conditions;[91] in this case, interparticle bonding permits no separation of the unit layers within the stacks. Depending upon the environment, swelling clays such as montmorillonite and vermiculite may exist as independent unit layers or as stacks of layers in particles. In general, the amount of face-to-face aggregation decreases and the interlayer spacing increases with decreasing solids concentration, increasing energy of interaction of the interlayer counterions with the substance adsorbed in the interlayer regions, decreasing electrolyte concentration, and decreasing affinity of the interlayer counterions for the clay surface (ref 32, 50–52, 56–58, 63–68, 70, 71, 77, 82, 92–98). These phenomena can be studied by means of X-ray diffraction and swelling pressure techniques, in conjunction with vapor or liquid adsorption measurements, and will be considered more fully in the sections on clay–water and clay–cation interactions.

Some turbidimetric studies on clay suspensions have been interpreted in terms of face-to-face aggregation. In general, the turbidity of a swelling clay suspension increases with increasing affinity of the counterions for the clay surface (ref 70–73, 75, 77, 78, 92, 95, 99); some authors have taken this to mean that the particle size increases because of an increase in the amount of face-to-face stacking of the unit layers. Certain objections to such conclusions can be raised. Laffer, *et al.*,[72,78] criticize the use of equations derived for small, monodisperse spheres to light scattering data from polydisperse clays; they present electron microscope and birefringence data which suggest that during the course of face-to-face aggregation considerable lateral growth also occurs owing to partial overlap of the layers. As a result, irregular lamellae are produced, the lateral dimensions of which are considerably larger than those of the original particles. In addition, it should be noted that simple stacking of unit layers would decrease the number density of particles in suspension without greatly altering the major dimensions; such aggregation would therefore be expected to result in decreased turbidity with increasing face-to-face association.

Light scattering and viscosity measurements on montmorillonite in the pH range 6–13[79] were interpreted in terms of ribbon-like edge-to-edge associated flocs, whereas light scattering studies on similar systems in electric fields[74,81] led to the conclusion that the "ribbons" were caused by edge-to-face association. However, it is doubtful whether the accuracy of the theory used warrants differentiation between the two modes of association.

The degree of edge-to-face or edge-to-edge flocculation in clay suspension can be estimated from rheological studies (ref 6, 8, 12, 13, 16, 21, 24, 38, 85, 86, 88, 100, 101). The formation of voluminous card-house flocs, or extended chains, will increase the viscosity of the suspension over that observed before the flocculation took place. In neutral or acid media, flocculation occurs primarily *via* edge-to-face association,[6,12,13,21] which results in card-house flocs giving high values of the viscosity and a finite yield value in concentrated sols.[85,88] Maximum viscosity is observed in the neutral pH range[12,13,16,38] where the edges are almost or completely neutralized by hydroxide ions; this has been interpreted in terms of ribbon-like flocs formed from edge-to-face[16] or edge-to-edge[12,38,79] association. Increased concentrations of base result in complete deflocculation and reduced viscosities. Adsorption of anions other than hydroxyl (ref 8, 20, 21, 23, 24, 101–104), as well as of anionic polymers (ref 24, 100, 101, 105, 106), and even of small negatively charged particles (ref 21) can disrupt edge-to-face association by neutralization of the positive edges and cause deflocculation.

The addition of neutral electrolytes to flocculated clay suspensions also changes the viscosity. For example, with increasing salt concentrations, the viscosity of a flocculated montmorillonite suspension first decreases because of deflocculation,[13,85,88] then increases again because of reflocculation.[86,88] van Olphen[3] suggests that relatively low concentrations of electrolyte cause deflocculation by reducing edge-to-face attraction by compression of the double layers; apparently, the effect of double layer compression on face-to-face and edge-to-edge repulsion is insufficient at these electrolyte concentrations to cause significant additional aggregation through these kinds of interactions. Additional electrolyte will further compress the double layers and may again result in the formation of flocs; the modes of bonding will vary from case to case, depending upon the pH, the nature of the electrolyte, and the kind of clay in the system.

O'Brien and coworkers[83,84] have developed a freeze-drying technique for preparing electron microscope specimens of flocculated clays. Electron micrographs obtained confirm edge-to-face structure in systems in which their presence had previously been assumed.

Permeability studies[89] indicate that the porosity of kaolinite flocs is greatest in acidic media. Intermediate porosities were observed at alkaline pH values in the presence of relatively high electrolyte concentrations; the lowest porosities occurred in salt-free sediments from alkaline media. These data are in good agreement with the results of the rheological studies previously mentioned.

Particle–particle interactions will be considered further in sections dealing with colloid stability and interactions of clays with water and solute species.

D. Electrokinetic Phenomena

Electrokinetic techniques, in particular electrophoresis, are used commonly in the studies of colloidal dispersions. In principle, the experimental data (such as the electrophoretic mobility, *i.e.*, the velocity of particles per unit field strength) can be used to calculate the potential at the plane of shear (the slipping plane), which can then be related to surface potential and/or to particle charge density. A rather comprehensive review of electrokinetic phenomena has been prepared by Derjaguin and Dukhin.[107]

Although electrokinetic measurements on clay suspensions have been reported frequently, considerable difficulties are encountered if the results are to be interpreted in terms of the surface potentials or charge densities. This is due in part to the fact that the simplest equations relating mobilities to the electrokinetic potential assume spherical particle shape. Morrison[108] has shown that the well-known Smoluchowski equation for calculating the zeta (ζ) potential (the potential at the slipping plane) may be applied, under certain conditions, to particles of arbitrary shapes. However, more serious objection to the use of Smoluchowski's equation when clay suspensions are involved lies in the heterogeneity of particle charge of the latter. The positive charges on the edges of the platelets will reduce the net negative charge of the particle, resulting in a lower negative mobility. ζ potentials calculated from these mobilities cannot accurately represent the potential at the shear plane in the vicinity of the negative faces;[103] theoretical considerations show that the potential at the plane of shear must be somewhat more negative than the ζ potential calculated from the electrophoretic mobility.[15,109] Indeed, it is questionable whether one can even justifiably speak of a potential at the plane of shear for a particle which bears positive and negative charges on different parts of its surface. This difficulty may be overcome by making all electrokinetic measurements at high pH, or in the presence of a strongly adsorbed anion; under these conditions, the edges of the particles are neutral or even negatively charged.

The fact that clays have appreciable surface conductivities (ref 40–42, 60, 110–117) further restricts the use of the Smoluchowski equation, which in principle, applies only to systems whose particles possess negligibly small surface conductivity (ref 108).

Studies of the influence of pH on the charge on clay particles indicate that, in general, the negative mobility of the particles increases with increasing pH (ref 13, 16, 18, 118–121). Anion adsorption has a similar effect on increasing the negative mobility of clay particles as does raising the pH (ref 13, 15, 16, 106, 121–124).

The influence of cationic species on the electrokinetic properties of clay sols also has been studied. In general, the particles appear to become less negative with increasing affinity of the positive ions for the clay surface (ref 60, 94, 119, 125–128). The negative mobility changes little with the concentration of simple cations of low charge (ref 118, 123, 125, 126), but may be reversed to positive by strongly adsorbed and/or highly charged cations (ref 118, 125, 126, 129–134).

II. Interactions at the Clay Surface

A. Clay–Water Interface

There are two principal manners in which a clay particle can be hydrated. Firstly, there is hydration of the surface of the crystal lattice. Three-layer clays, such as montmorillonite and vermiculite, present mainly a siloxane surface to the environment, whereas the faces of two-layer clays like kaolinite are siloxane and hydroxylated alumina, respectively, both of which structures are capable of interacting with water molecules. Secondly, the positive counterions may also be hydrated. Indeed, it is often difficult to separate the foci of hydration, as water bonded primarily to the particle surface may be greatly influenced in its orientation, mode of bonding, and energy of interactions with clay by the presence of neighboring cations.

Adsorption of water vapor on clay mineral surfaces appears to be an exothermic process, the enthalpy of adsorption being negative in all systems in which the counterions are metal cations.[28,64,135–138] The entropy of adsorption depends on the water content and the nature of the counterion. Kijne[135] and Kohl, *et al.*,[136] report that the first water adsorbed on lithium kaolinite and lithium montmorillonite has a greater entropy than liquid water, but the entropy of the adsorbed water drops to less than that of liquid water before monolayer coverage is complete. Water adsorbed onto the analogous sodium and calcium saturated clays has a lower entropy than the free liquid for all amounts of coverage.[135] Other reports show that water adsorbed on montmorillonite tends to have a lower entropy than liquid water,[137,139] and according to van Olphen, *et al.*, the entropy of adsorption of water on sodium vermiculite is negative.[140,141] Finally, at low water contents (about 0.07 monolayer), the entropy of water adsorbed on kaolinite is approximately that of ice, although at slightly higher coverages (up to two molecular layers of adsorbed water) it is greater than that of the free liquid.[142]

The separate contributions of the surface and of the counterions to these thermodynamic quantities are difficult to evaluate. There is a definite dependence of enthalpy and entropy on the counterion present; it has been observed[28,138,140,143] that the amount of adsorbed water on clay and the heat of adsorption are greater for samples with easily hydrated counterions. The net energy of hydration of the clay particles is less than the hydration energies of the cations in bulk solution.[136,140,144] Although lithium hydrates much more strongly in solution than does cesium or rubidium, Mooney, *et al.*,[28] report that their lithium saturated montmorillonite adsorbed only slightly more water vapor per counterion than did the analogous cesium or rubidium clays.

Water adsorbed on clay particles appears to retain many properties of liquid water. It exhibits a similar surface tension,[136] its infrared spectrum resembles that of liquid water,[145] and it dissolves organic and inorganic species and permits their diffusion,[111,146] although at rates lower than in bulk solution. The density of adsorbed water was reported to be lower than that of liquid water;[147–149] however, this property seems to depend on the amount of the water at the interface and on the distance from the clay surface. The density of water near a montmorillonite surface apparently decreases to a minimum (approximately equal to the density of ice) at about 10 Å from the surface.[29,148,149] At lower water contents the density was found to be equal to[150] or even greater than[29,142] that of water. Also, the density of the first two layers of water adsorbed on vermiculite is higher than that of water.[141] Many investigations have shown that the viscosity of adsorbed water is considerably higher than that of bulk water.[114,115,151–155] It drops rapidly beyond the first three or four layers of adsorbed water,[156] but the first layer exhibits a viscosity so great that it may be considered to be immobile.[152,157] This first layer has been described as ice-like,[151,158] and its has been called a surface hydrate.[159]

Low-temperature studies (ref 147, 148, 155, 160–164) indicate that water adsorbed on clay surfaces retains liquid-like properties at temperatures below 0°, *i.e.*, as low as $-10°$[148,155] or even $-16°$.[163] Martin[142] discussed this extensively and concluded that the first few layers of adsorbed water behave more like a two-dimensional fluid than like a solid.

Adsorption onto clay surfaces affects the properties of water in other ways as well. Derjaguin, *et al.*,[165] claim that the dielectric constant of the first one or two interlayers of water adsorbed by sodium montmorillonite is about one-half its normal value. There is ample evidence that water is much more extensively dissociated in the interlayer regions than in bulk.[39,166] Nmr studies indicate a degree of dissociation of interlayer water 10^6–10^7 times greater than in bulk water;[167,168] similarly, from conductance data it appears that about 1% of the adsorbed water is ionized.[169] This increased dissociation could partially account for the increased entropy of adsorbed water observed in some cases.[135,136,142]

At low surface coverage the heat of desorption of water from montmorillonite is approximately 12–13 kcal/mol;[65,135] this suggests that the adsorption may not be physical. On the other hand, it was observed that the amount of water adsorbed on the clay increased as the temperature decreased[28,65] which is the opposite of what is usually expected in chemisorption. Brunauer[170] has suggested that ion–dipole interactions account for the adsorption of water vapor on materials similar to clays, and the forces involved are borderline between those responsible for physical and chemical adsorption, respectively.

The role of hydrogen bonding in water adsorption by clays is not clear. There are several proponents of water hydrogen-bonded to siloxane of clay surfaces.[58,65,171–178] On the other hand, Kijne[135] maintains that no stable hydrogen bonds are formed with the oxygens of the siloxane surface, and it has been acknowledged[149,177,179] that most hydrogen bonds between water and the clay surface are quite weak. Such bonds would be more likely to occur at less than monolayer coverage. Such isolated adsorbed water molecules would be unable to form hydrogen bonds with other water molecules either at high coverage or in aqueous suspension. Water should hydrogen bond readily to the hydroxylated alumina surface of kaolinite-type clays.[175]

It has been noted (see Table I) that considerably different values for the BET surface areas for expanding three-layer clays were obtained from the nitrogen and water vapor adsorption isotherms.[28,65] Furthermore, water vapor gives stepwise isotherms with significant hysteresis between the adsorption and desorption branches,[28,64,65] whereas nitrogen isotherms exhibit neither hysteresis nor a stepwise shape. The adsorption studies of water vapor on montmorillonites and vermiculites saturated with mono-, di-, tri-, and tetravalent metal cations and hydrogen showed that the amount of water corresponding to each subsequent plateau in the isotherm is approximately equivalent to one, two, or three layers of water between adjacent unit layers (ref 28, 64, 65, 140, 143–145, 171). X-Ray studies with homoionic clays indicate that the distance between adjacent unit layers increases in a stepwise manner, the separation between steps being 2.5–3 Å.[28,64–67,140] These steps in the interlayer distance occur at the same water contents and relative pressures of water vapor as the inflections in the adsorption isotherms. One concludes that water vapor can penetrate between the unit layers of a montmorillonite tactoid, forcing them apart by the equivalent of a layer of water at a time.

Hence, it appears that water vapor adsorbs onto all the surfaces of expanding clays both internal and external. Since the adsorption of nitrogen causes no change in the interlayer spacing of these clays,[180] it is further concluded that nitrogen molecules adsorb on the external surfaces only and cannot penetrate between the unit layers.

Adsorption of water onto nonexpanding clays such as kaolinite occurs chiefly on the external surfaces, as indicated by the agreement of the BET surface areas obtained from nitrogen and water vapor adsorption data.[28,181]

The concentration of solids in a clay–water slurry may also affect the amount of liquid water adsorbed by clay particles. Below about 30% the clay concentration has little effect on the amount of water associated with the particles. At higher solid contents the amount of adsorbed water per unit weight of clay decreases; at these concentrations all of the water present in the system is bound by the clay.[66–68]

Numerous studies have been reported dealing with the effect of various counterions on the adsorption of water on clays (ref 32, 40, 50, 52, 64–67, 135, 140, 145, 171, 175, 176, 182). For a given counterion charge, the amount of water adsorbed by a clay becomes higher as the hydration energy of the counterion increases. Whereas clays with polyvalent counterions may adsorb more water vapor than those with univalent cations,[32,64,135,176] in aqueous pastes or suspensions the amount of water associated with the clay particles is greater when the counterion is univalent.[68,69,175] In montmorillonite clays, the amount of water adsorbed between the unit layers (ref 32, 58, 63, 66, 67) and the related degree of aggregation of particles in suspension (ref 21, 50–52, 56, 57, 63, 72, 77, 85, 92, 93, 95, 97, 98) exemplify such behavior. In general, in the presence of univalent cations with small unhydrated radii, *e.g.*, hydrogen, lithium, and sodium, a stepwise swelling is observed until there are about four interlamellar water layers; beyond this, swelling is continuous. With large univalent cations such as potassium, ammonium, and cesium, the clay adsorbs up to two or sometimes three interlayers of water. Similarly, with divalent ions (*i.e.*, magnesium, calcium, and barium) and trivalent aluminum, two or three interlayers are observed.[32,64,66,68]

The swelling of expanding clays, upon adsorption of water, is believed to occur as follows (ref 3, 9, 49, 50, 52, 57, 58, 66–68, 135, 144, 175, 176, 183). The initial stepwise expansion is caused by hydration of the internal surfaces of the clay and of the interlayer cations. When several layers of water have been adsorbed between the unit layers, osmotic forces caused by the relatively high ionic concentrations between the layers may lead to a continuous swelling. The degree of swelling under various conditions depends upon the charge on the clay lattice, the nature of the counterions, the hydration energies involved, the bulk ionic strength, and the total water content. Whether or not a clay undergoes this continuous osmotic swelling depends on whether hydration forces can expand the clay to the point at which repulsive and osmotic forces can overcome any attractive forces present. Similarly, if the counterions are held relatively strongly to the two surfaces, the interlayer attraction will be great enough to prevent osmotic swelling. Finally, the unit layer separation of a clay undergoing osmotic swelling will ultimately be limited by the amount of water in the system.

An indication of the extent of swelling in an aqueous clay suspension can be obtained from the amount of face-to-face aggregation of the unit layers, as such aggregation is directly related to the ease of separation of the layers. Thus, montmorillonites which swell most easily in water are also the least aggregated; the order of aggregation is Li $<$ Na $<$ K $<$ Rb $<$ NH_4 $<$ Cs $<$ Mg $<$ Ca $<$ Ba montmorillonite (ref 70, 73, 77, 92, 93, 97). Similar effects have been observed with mixtures of Na and Ca montmorillonite.[82,95]

B. Inorganic Cations

The influence of cation hydration, ionic size, charge, and polarizability has been studied in regard to the strength of the bonding forces with clays (ref 40–42, 58, 86, 110, 159). Various approaches have yielded the same or very similar orders with respect to the relative strength of interactions of inorganic cations with the surfaces of various clays. From conductance data this order for a montmorillonite surface is $Li^+ < Na^+ < K^+ < Rb^+ < Ca^{2+} < Cs^+$.[40–42] The association of counterions with montmorillonite and kaolinite was found to increase as $Na^+ < K^+ < Mg^{2+} < Ca^{2+}$ [159] and $Li^+ < Na^+ < K^+ < NH_4^+$,[25] respectively. The strength of the clay–cation bond appears to increase linearly with increasing polarizability of the cation, *i.e.*, $Na^+ < K^+ < Rb^+ < Cs^+$.[110] These trends are reflected in the preference for ion exchange of inorganic cations onto clay minerals.

Three generalizations may be made concerning the tendency of a cation to exchange onto a negative surface. The exchangeability increases (a) with decreasing hydrated radius and increasing polarizability, (b) with increasing counterion charge, and (c) with decreasing ease of cation hydration. Only in cases where some specific interactions take place, the above criteria may not strictly apply. In agreement with the above observations, the order of increasing preference of alkali ions for ion exchange onto montmorillonite (ref 43, 75, 184–204), vermiculite (ref 190, 205), and kaolinite (ref 191, 197, 206, 207) is $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Thermodynamic data for the exchange of these cations on montmorillonite are given in Table II.

The measurements of exchange of ammonium ion are complicated by physical adsorption of ammonia[208] and fixation of ammonium.[209] It was reported that ammonium ion is held more strongly than sodium ion,[210] or even rubidium ion.[211] Another observed order of preference is $Li^+ < Na^+ < NH_4^+ < K^+$,[198,209] although there are cases in which NH_4^+ seems to be more strongly held than K^+,[190,205,212] but less so than Rb^+.[190,205] Indeed, there are indications that ammonium ion may be as strongly bound by clays as divalent cations.[213–15]

TABLE II. Thermodynamic Data for Monovalent Cation Exchange of Montmorillonite (25°)

	Wyoming bentonite[198,201] cec = 92 mequiv/100 g			Chambers montmorillonite[202] cec = 123 mequiv/100 g		
Reaction	$\Delta G°$, cal/mol	$\Delta H°$, cal/mol	$\Delta S°$, eu	$\Delta G°$, cal/mol	$\Delta H°$, cal/mol	$\Delta S°$, eu
Li → Na	−48	−150	−0.5	−80	−111	−0.1
Li → K	−490	−712	−0.7		−1156	
Li → Cs		−2554		−2218	−2472	−0.8
Na → K	−306	−605	−1.0	−725	−1161	−1.5
Na → Rb	−634			−1347	−1920	−1.9
Na → Cs	−1081	−2557	−4.9	−1886	−2648	−2.6
K → Cs		−1957			−2049	
Rb → Cs	−575			−809	−1081	−0.9

Similarly, the exchange of hydrogen ion is difficult to measure, because it attacks the clay lattice, freeing aluminum and magnesium ions which may be taken up by the exchange sites (ref 3f, 17, 206, 216–221); consequently, some of the exchange attributed to hydrogen ion could be caused by metal ions dissolved from the clay. This is most likely the case in work indicating that hydrogen ion is apparently preferred over some divalent cations in ion exchange on montmorillonite and clay soils[189,212,222] and over cesium on vermiculite.[205] Other investigations show a less pronounced preference for hydrogen ion; relative orders of exchange on montmorillonite reported are $H^+ < Cs^+$,[195] $K^+ < H^+ < Ca^{2+}$,[75] and $K^+ < NH_4^+ < H^+ < Mg^{2+}$.[203] Under conditions which apparently minimize dissolution of the clay by acid attack, the corresponding orders were $H^+ < Na^+ < K^+$ [186] and $Na^+ < H^+ < NH_4^+$.[210] Although the differences may still, at least in part, be due to dissolution of the clay, it is possible that some specific interactions could be the reason for the inconsistencies. Kown and Ewing[223] have observed that hydrogen–sodium and hydrogen–strontium exchange do not follow the simple mass action law; they conclude that additional factors other than simple ionic attractions are involved (*e.g.*, protonation of lattice hydroxyls, interactions with broken bonds at the edges, etc.). It was also noted that the preference for the exchange of hydrogen ions may decrease with increasing clay concentration.[224]

The order of exchange of alkaline earth ions on clays has generally been observed to be $Mg^{2+} < Mn^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ (ref 186, 189, 206, 213, 214, 223, 225–233). The reverse order is sometimes found in the case of vermiculite,[230,234,235] and approximately the same exchange for Mn^{2+} and Ca^{2+} has been reported for montmorillonite.[236] Furthermore, on montmorillonite and aluminum-saturated kaolinite Uskova and coworkers[206] observed the expected exchange preference $Ca^{2+} < Sr^{2+} < Ba^{2+}$, whereas their H-kaolinite exhibited the order $Sr^{2+} < Ca^{2+} < Ba^{2+}$. The preferential exchange of strontium to calcium on some clays and soils has been attributed to the presence of organic matter, which binds strontium more strongly.[72] The inversion of exchange orders of alkaline earth ions at high pH[184] ($Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$) has been explained by hydrolysis; the more readily is the ion hydrolyzed, the better it is adsorbed. This was substantiated by work with cobalt salts in clay suspensions which showed that adsorption of cobalt(II) ions increased with pH.[237,238] The fact that calcium ions are taken up in their hydroxylated form by montmorillonite and kaolinite was also suggested by Diamond and Kinter.[239]

Several investigations deal with the exchangeability of divalent transition metal cations on clays, for which orders $Mn^{2+} \simeq Ni^{2+} \simeq Fe^{2+} < Co^{2+} < Zn^{2+} < Cu^{2+}$,[213,240] $Zn^{2+} < Mn^{2+} \leq Ni^{2+} < Co^{2+} < Cu^{2+}$,[241] $Ca^{2+} < Co(II)^{2+}$,[222,242] and $Ni^{2+} < Ba^{2+}$ [232] have been reported.

Studies comparing the exchange of mono-, di-, and trivalent cations on clay have shown, in principle, a preference for cations of higher charge (ref 36, 75, 185, 186, 189, 193–195, 203, 206, 212, 214, 225, 229–231, 242–247). However, this trend is not always followed, especially when a strongly held monovalent ion is compared with a relatively weakly held divalent ion. As mentioned above, ammonium[213–215] and hydrogen ions[91,212,222] are sometimes preferred over more highly charged cations, most likely because of specific interactions. Cesium and rubidium have also shown anomalous behavior. For example, Cs^+ was exchanged more strongly than Ca^{2+} on a mica sample,[244] and similarly on montmorillonite,[195] but in the latter case this was observed only if the Cs^+ concentration was sufficiently low ($<10^{-3}$ *M*). Uskova and coworkers[206] found that a predominantly hydrogen saturated kaolinite exhibited the expected preference of divalent over monovalent cations, whereas the same clay in the aluminum form showed a greater preference for rubidium and cesium ions than for divalent calcium, strontium, or barium.

Studies of the effect of the salt concentration on the exchangeability of cations on an aluminum montmorillonite[185] showed that in dilute solutions the order was $Na^+ < K^+ < Ca^{2+}$; as the total normality of the solution increased, the relative adsorptivity of calcium decreased, until at 2 *N* the order was $Ca^{2+} < Na^+ < K^+$. A similar trend was observed for the adsorption of divalent cations on montmorillonite.[231]

Potassium may on occasion be taken up in preference to multivalent cations. The ease of removal of aluminum counterions from montmorillonite and kaolinite by various cations was found to be $Na^+ < Ca^{2+} < K^+$.[193] Similarly Foscolos[186] established that aluminum montmorillonites preferred potassium over various polyvalent cations, and also noted an effect of cation exchange capacity (cec) on the order of exchange preference; for a clay with a cec of 90 mequiv/g, this was $H^+ < Na^+ < Mg^{2+} < Ca^{2+} < K^+ < Al^{3+}$, whereas a similar clay with a cec of 125 mequiv/g exhibited the order $H^+ < Na^+ < Mg^{2+} < Ca^{2+} < Al^{3+} < K^+$. Some soil clays have exhibited the preference $Ca^{2+} < K^+$.[247] It has been suggested[3] that this effect is partly due to the size of the unhydrated potassium ion (1.33 Å), which permits it to take up a very favorable interlayer position.

Irreversible uptake of cations (*i.e.*, fixation) can sometimes result in anomalous ion exchange behavior. This is especially prevalent with vermiculite, which can fix potassium, ammonium, cesium, and rubidium.[190,198,248–251] Montmorillonite is more resistant to counterion fixation than vermiculite,[190,194,243,252] but some such bonding of potassium and cesium may take place.[249–251,253] Cation fixation and lattice collapse are often closely related; that is, the unit layers are held tightly together, rendering the interlayer region relatively inaccessible with respect to ion exchange. Interlayer adsorption of nonionic molecules (*e.g.*, water) is also hindered in collapsed lattices. In such cases, the ion exchange preference order of monovalent cations appears to be reversed;[190,198] it was suggested that those cations with smaller unhydrated radii can more easily penetrate between the layers to exchange with some of the "fixed" ions. Once in the interlayer region, the new counterions readily separate the collapsed layers by picking up water of hydration; this swelling enhances further exchange of the fixed cations.

Other cations may also be fixed by clays. When a lithium kaolinite is dehydrated, the small unhydrated lithium ions subside into lattice vacancies, becoming very difficult to hydrate or exchange.[144,254] Clay minerals can also take up nonexchangeable hydroxylated aluminum species.[255-258] In addition, Hodgson and Tiller[213,240] report that a portion of the cobalt(II) sorbed by montmorillonite is fixed; they suggest that the cobalt either enters into the crystal lattice or is occluded *via* precipitation as cobalt hydroxide.

A number of studies have been reported on the surface diffusion of cations on clays. For cations on montmorillonite the order of surface diffusion rates is $\mathrm{Na^+} > \mathrm{K^+} > \mathrm{Cs^+}$, reflecting the energies of activation of diffusion, which follow the order $\mathrm{Na^+} < \mathrm{K^+} < \mathrm{Cs^+}$.[110-112] In other work, however, the relative activation energies for surface diffusion on homoionic montmorillonite were found to be $\mathrm{K^+} < \mathrm{Na^+} < \mathrm{Li^+}$ or $\mathrm{K^+} < \mathrm{Li^+} < \mathrm{Na^+}$, depending on the source of the clay.[113,114] The increase in viscosity of the water near the surface is considered to be mostly responsible for this activation energy; good correlation was found between the energies of activation for cation diffusion, and for surface diffusion of water on different ionic forms of various clays.[114,115] Lower activation energies for surface diffusion of counterions were found in those clays in which the surface water was more mobile; it would seem that when the surface water is freer to move it offers less hindrance to the mobility of cations along the surface. Relative rates of diffusion of certain divalent transition metal cations on kaolinite and montmorillonite[117] were found to be $\mathrm{Cu^{2+}} < \mathrm{Mn^{2+}} < \mathrm{Zn^{2+}}$, which is opposite to the order for diffusion rates in solution; the rate of surface diffusion for the same cations decreased with increasing cation exchange capacity of the clay. Finally, it has been found that sodium ion diffuses along clay surfaces much more readily than does calcium ion.[111,116]

Electrical conductance of counterions shows a decrease due to interaction with the clay surface (as compared with conductance in bulk solution), the relative decrease being in the order $\mathrm{Li^+} < \mathrm{Na^+} < \mathrm{K^+} < \mathrm{Cs^+}$. Consequently, the fraction of counterions contributing to conductance was $\mathrm{Li^+} > \mathrm{Na^+} > \mathrm{K^+} > \mathrm{Cs^+}$.[41,42]

Thus, the evidence shows that the following factors affect the interactions between inorganic cations and clay surfaces: (1) the unhydrated radius, (2) the charge, (3) the energy hydration, and (4) specific interactions (*e.g.*, $\mathrm{H^+}$, $\mathrm{NH_4{}^+}$). The larger are the first two parameters and the lower is the third, the stronger are the interactions. The first three factors are those which generally enhance bonding between a cation and any negatively charged substrate; the fourth is more specifically characteristic of cation interactions with clays.

C. Anions

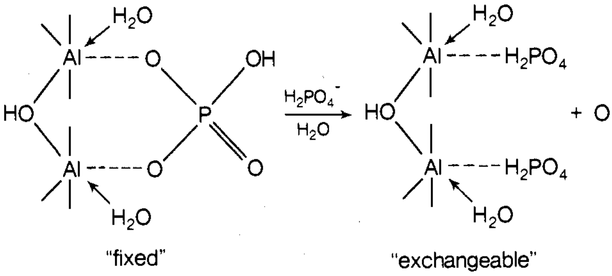
The surface charge properties of clays play a special role in their interactions with anions. The strong negative charge of the faces repels them, whereas the weak positive charge on edges attracts anions. In addition, specific bonding with cations of the clay surface may also occur. The nature of charge distribution on clay explains why, under various conditions, both negative and positive adsorption of anions has been reported.

Bolt and Warkentin[47] measured the negative adsorption of chloride ions by montmorillonite, but the amount found was lower than predicted by the double layer theory. This was explained by the neglect of making corrections for activities and for positive adsorption on edges. The use of chloride exclusion by homoionic montmorillonite to determine the specific surface areas gave anomalously low results (ref 22, 31, 33, 34, 46), which may have been due to the aggregation of clay particles, and also due to positive adsorption on edges which had not been taken into consideration. Positive adsorption of chloride ions on clay was found to take place at pH ≤ 6.[18,104] Similarly, a small amount of positive adsorption of sulfate ions on montmorillonite was detected[5] and attributed to the uptake of these ions by the edges of the platelets.

Phosphate ions have a particularly strong effect on the properties of clay dispersions. This involves electrokinetic, stability, and rheological phenomena.

Lyons[8] reports that the adsorption of triphosphate on kaolinite follows a Langmuir-type isotherm. There is a direct correlation between the point of maximum uptake of the anion and the amount of triphosphate required for full deflocculation of the sol by neutralization of edge charge; an increase in negative electrophoretic mobility of the clay was also observed under these conditions. From his adsorption measurements, Lyons estimates that approximately one-third of the alumina-like edge area is covered with triphosphate at saturation. An increase in negative electrophoretic mobility was also observed with kaolinite in the presence of phosphate ions[15,16,122,123] which was simultaneously accompanied by a decrease in the yield value of the system.[16] A similar effect on the viscosity of montmorillonite was reported in the presence of polymetaphosphates.[102]

Kafkafki and coworkers[7,259] have observed that not all the phosphate adsorbed by kaolinite is isotopically exchangeable. They conclude that there are two modes of phosphate bonding to the edge of clay particles



Preliminary tests indicate that montmorillonite behaves in a similar manner.

In studies of the desorption of phosphate from kaolinite in the presence of various anions, Nagarajah, *et al.*,[260] observed that chloride displaces little or no phosphate. Citrate and bicarbonate ions displace phosphate; however, the equilibrium amount of phosphate adsorbed depends on the order of addition of phosphate and the competing anion to the clay suspension. If phosphate is added first, it is retained in greater quantities than if it is added at the same time as, or after, the other anion.

Michaels and Bolger[13] have titrated a salt washed kaolinite, in which the counterions are presumably hydrogen, sodium, and (at the edges) chloride ions, with sodium hydroxide and hydrochloric acid. The observed coincidence of a kink in the titration curve at pH 7.8 with the complete deflocculation of the clay is interpreted as complete neutralization of positive edge charges (by hydroxide ion) at that pH. They also report that the anion exchange capacity of kaolinite vanishes as the pH is raised above 6.

Bingham and coworkers[261] have studied the retention of acetate ion by montmorillonite. They found that a maximum of about 0.5 mequiv of acetate/g of clay was retained at pH <6; between pH 6 and 8 the amount of acetate adsorbed dropped to about one-tenth of this value. This compares favorably with the titration work of Michaels and Bolger;[13] at pH >6 competition with hydroxide ion would lead to a reduction in acetate adsorption. The amount of acetate retained was independent of the cation present for sodium and ammonium ions. When the OAc^--clay complex was washed with solutions of the ammonium or potassium salts of various anions, the effectiveness of removing acetate was $NO_3^- \approx Cl^- < SO_4^{2-} < H_2PO_4^- < OH^- \approx F^-$, independent of the cation. Furthermore, the amount of phosphate retained by the clay was equal to the amount of acetate it replaced, indicating a stoichiometric exchange.

Studies of anion exchange cited by Wayman[29] are in good agreement with the work of Bingham, *et al.* He reports the preference for anion exchange on clays as $CNS^- < I^- < NO_3^- < Br^- \approx CH_3COO^- < Cl^- < H_2PO_4^- < OH^- < F^-$.

Deflocculation of clays can be accomplished by a variety of anionic species when these adsorb in sufficient amounts to neutralize the edge charge. For example, hexadecyl sulfate at pH ~3 renders kaolinite particles more negative and causes a breakup of flocs.[103] Similar effects were observed when ferrochrome lignosulfonates were added to montmorillonite.[24] van Olphen[102] found that metasilicate, polymetaphosphate, and oxalate ions stabilize sodium and calcium montmorillonites; this was attributed to edge charge neutralization, to a decrease in sodium ion activity, and to the inactivation of strongly flocculating calcium ions by complex formation or precipitation.

D. Organic Molecules

Association of an organic molecule with a clay particle may take place in several ways. The molecule may be adsorbed on the clay lattice by ion–dipole forces, by van der Waals forces, or by hydrogen bonding. It may also complex with a counterion of the clay, or, if it is ionized, it may undergo cation or anion exchange with the original counterions.

A number of studies have been reported on interactions of low molecular weight alcohols with clays saturated with inorganic ions.[172,173,262] Infrared data on deuterated methanol vapor adsorbed on montmorillonite powder[172] indicate that the alcohol molecules not only are hydrogen bonded to surface oxygens of the clay lattice, but also interact specifically *via* a partial electron donation from the oxygen of the methanol hydroxyl to the counterions on the surface. Similar observations have been made for the adsorption of 1-propanol on montmorillonite.[173] The degree of donor–acceptor bonding increases with increasing polarizing power of the cation, that is, $Li^+ > Na^+ > Cs^+$,[173] and with the ability of the cation to form coordinate bonds, *i.e.*, Cu^{2+}, $Co^{2+} > Na^+$.[172] For the interaction of ethanol with clay counterions, the following order was reported: $Ca^{2+} > Ba^{2+} > Na^+ > K^+$.[262]

Adsorption studies of ethanol and ethylene glycol on montmorillonite led Dowdy and Mortland[263,264] to conclude that hydrogen bonds with the clay surface are formed only if the alcohol cannot form a coordinate bond with a counterion, either because the coordination sphere of the cation is saturated, or because the cation does not readily enter into such bonding. Thus, the degree of interaction of ethanol with various counterions was found to be NH_4^+, $Na^+ < Ca^{2+} < Cu^{2+} < Al^{3+}$;[264] with ethylene glycol, the order of interaction with Cu^{2+} and Al^{3+} is reversed, the higher charge of the aluminum probably being outweighed by the greater tendency of copper(II) ions to form coordinate bonds.[263]

The interactions of ethanol and methanol with the counterions of a montmorillonite clay were also followed by electrical conductivity measurements.[42] The conductances of lithium, sodium, and potassium ions undergo greater relative reductions from association with the clay surface when pastes contain alcohol rather than water as the dispersion liquid. Whereas the decrease of conductance in water is in the order $Li^+ < Na^+ < K^+$, alcohol appears to affect the strength of the interaction between counterion and clay approximately equally for all of these cations. Methanol renders 90% of these counterions immobile, ethanol 95%, whereas in water only 36% of the sodium counterions do not contribute to electrical conductance.

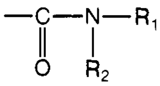
Brindley and Ray[265] have studied the basal spacing of calcium montmorillonite in the presence of straight chain alcohols with 2 to 18 carbon atoms. They conclude that mono- and bilayers are formed between the unit layers of the clay with the chain of the alcohol parallel to the surface of the clay, and suggest that hydrogen bonds are formed between alcoholic hydroxyls and siloxane oxygens.

Desorption studies of glycerol from kaolinite and montmorillonite resulted in enthalpies of desorption of 40 and 55 kcal/mol, respectively.[266] The greater heat of desorption from montmorillonite is believed to be caused by the higher cation exchange capacity and the necessity of removing glycerol from the interlayer regions.

Measurements of the adsorption of ketones on montmorillonite indicate that any bonding of these compounds directly to the clay lattice is due to weak physical adsorption forces, and that the primary source of uptake is through interaction with the counterions.[267] Depending on the water content and the hydration energy of the cation, the ketone appears either to bond directly to the cation *via* ion–dipole or coordinate bond forces through the carbonyl oxygen, or to be bound through hydrogen bonding to a water molecule in the first hydration layer, *i.e.*, through formation of a water bridge between the ketone and the metal ion. When the counterion is ammonium, the primary interaction appears to be the hydrogen bonding between ammonium and the carbonyl oxygen on the ketone.

Infrared spectra indicate that the adsorption of acetonitrile onto montmorillonite[174] is due almost entirely to interactions with counterions, as acetonitrile cannot bind strongly either with the clay surface or with itself. The mode of bonding is believed to be of a donor–acceptor type originating from donation to the cation of the unshared electrons of the nitrogen of the $C \equiv N$ group. The strength of the complex increases as follows: $K^+ < Na^+ < Li^+ < Ca^{2+} < Cu^{2+} < Co^{2+}$; this is the same order as observed for the strength of alcohol–cation complexes.[172,173,262]

Adsorption of unprotonated amides (such as shown) onto montmorillonite seems to be primarily dependent upon the amide–counterion interactions through the car-



$$-\underset{\underset{O}{\|}}{C}-\underset{\underset{R_2}{|}}{N}-R_1$$

bonyl oxygen.[268,269] The observed order of the strength of the complex formed is $Na^+ < Ca^{2+} < Ni^{2+} < Al^{3+}$. Owing to the electron-donating effect of the alkyl groups, the interaction is more pronounced when R_1 and R_2 are alkyl groups rather than hydrogen; that is, the relative strength is primary < secondary < tertiary amides. Because of the smaller cec of kaolinite, amides are adsorbed onto this clay by hydrogen bonding of carbonyl oxygens to lattice hydroxyls and of hydrogens of the NH_2 group to siloxane oxygens.[270,271]

Adsorption of larger nonionic organic molecules[180,272,273] appears in some cases to be physical and nonspecific. The forces involved are probably hydrogen bonds between =NH and OH groups on the molecules and siloxane or aluminol oxygens on the clay. Such adsorbed molecules are readily desorbed by washing with water or aqueous salt solutions. On the other hand, Kodama and Schnitzer[274,275] have observed that the adsorption of an undissociated fulvic acid on montmorillonites increases in the following order of clay counterions: $Ni^{2+} < Fe^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Co^{2+} < Zn^{2+} < Na^{2+} < Cu^{2+} < Pb^{2+}$. This order appears to be determined by the observed stabilities of cation–fulvic acid complexes in solution and by the ease of dehydration of the interlayer counterions.

The fact that the water close to a montmorillonite surface is considerably more dissociated than in the bulk liquid state[167-169] explains a number of observations on the degree of ionization of organic acids and bases at clay–solution interfaces. For example, infrared studies in the presence of benzoic acid show that, at a measured pH of 7 (in bulk solution), the concentration of hydrogen ions near the montmorillonite surface is approximately 100 times higher than in bulk solution;[276] that is, the degree of dissociation at the clay surface corresponds to pH 5 or less. Thus, organic acids can adsorb onto clays in the undissociated form, even though bulk pH values would lead one to expect dissociation of the acid.[277] For the same reason, protonation of weak organic bases has been detected at or near a clay–water interface, when such behavior is not expected at the pH value measured in the suspending medium.[278-280] Infrared studies indicate that the first pyridine vapor sorbed by montmorillonite is protonated and bound as the pyridinium ion;[281] coordination of neutral molecules with metal counterions and the clay surface occurs only at higher coverages. The protonation of pyridine by montmorillonite in aqueous suspension was found to be sufficiently pronounced to suggest the use of pyridine as an indicator of surface acidity.[282] In slightly acidic media the infrared spectra of aniline and urea adsorbed onto montmorillonite are virtually identical with the spectra of their hydrochloride salts, indicating protonation.[277] Other studies suggest that some montmorillonites are capable of protonating organic bases with pK_a values up to 11.4.[252] It was observed that clays with negative sites in the tetrahedral (silica) sheet showed greater surface acidities than those whose negative sites are located in the octahedral (alumina) sheet, pointing to a relationship between negative field strength at the surface of the clay and the degree of dissociation of interfacial water.

The adsorption of amino acids and peptides on H-montmorillonite shows a Langmuir-type isotherm; such adsorption occurs primarily through ion exchange of the protonated molecules, although a small amount of the organic molecules is adsorbed beyond the cation exchange capacity.[283,284] With sodium and calcium clays the adsorption of these molecules appears to be physical, indicating less protonation; the negative free energy of adsorption increases with surface charge density of the clay and the number of monomers in the peptide chain.[283,284]

Weiss and coworkers[63,285-295] have made extensive studies of the orientation of organic cations and some nonionic organic compounds at the clay surface. They have found that the orientation of alkylammonium ions depends largely on their packing density which increases with increasing surface charge density of the clay. In relatively weakly charged clays such as montmorillonite and hectorite, the cations are oriented with the alkyl chains lying flat between the silica sheets. In clays with a moderate layer charge, *e.g.*, vermiculite, the chains are tilted with regard to the surface, and when the surface has a high charge density the increase in the number of adsorbed counterions causes their perpendicular orientation. In general, there is a linear relationship between interlayer spacing and surface charge density.[295] When long chain normal alcohols are adsorbed by the alkylammonium clays, they appear to take up positions similar in orientation to the counterions, with the OH group adjacent to the siloxane surface of the clay.

Laby and Walker[296] observed that alkylammonium ions with 8 to 18 carbon atoms formed complexes with vermiculite in which the alkyl chains in the interlayer regions were oriented at 56° to the surface. With shorter chains, there was room for the ions to lie parallel to the surface; hydrogen bonding in these systems was weak due to poor directionality. Suito *et al.*,[297] have also studied the orientation of long-chain organic compounds on bentonite; they found that octadecylamine was adsorbed in mono- or bilayers with the molecules oriented parallel to the surface, or, when more densely packed, in monolayers with vertical orientation of the molecules.

Thermodynamic data show that the negative free energy of exchange of *n*-alkylammonium ions on sodium montmorillonite increases with increasing chain length;[298] this reflects not only the clay–cation interactions, but also interactions between the alkyl chains of these cations.

It appears that the first portion of the cationic amine is adsorbed onto clay by ion exchange; if more amine is added to the system, the clay can take up as much again, to a maximum of about twice the cec.[299] The adsorption of surface active amines in excess of cec was also found to be dependent on the chain length.[272] The additional amine is not washed off with water; it would seem that the bonding of the excess cation involves ion–dipole and ion–ion interactions in addition to van der Waals forces. The adsorption of quaternary ammonium cations on kaolinite may be sufficiently strong to reverse the charge on the particles from negative to positive.[18,300] Reversal of charge and adsorption beyond the cec of montmorillonite sols have also been observed in the presence of tris(2,2′-dipyridyl)cobalt(III) ion and tris(1,10 phenanthroline)cobalt(III) ion.[118] Because of the large size of the chelates these complexes behave like bulky organic cations.

On the other hand, two dipyridinium-type herbicides (as halide salts) were taken up by montmorillonite and kaolinite by simple cation exchange; no additional cation was adsorbed once the negative sites on the clay were saturated.[180,273,301-303] Infrared data suggest that these herbicides are held to the clay primarily by ionic forces.[304]

Similar results were obtained in the titration of hydrogen-saturated montmorillonite and kaolinite with nicotine;[305] the protonated nicotine is adsorbed only up to the exchange capacity of the clay. These data support the observation that large organic cations tend to adsorb onto clays beyond the exchange capacity, whereas smaller cations do not.[306]

The general effect of saturating a clay with an organic cation is to render the clay surface hydrophobic. Montmorillonite and kaolinite saturated with alkylammonium cations separate from the water phase,[307] and under certain conditions organoclays may even spread on the surface of the water.[308] Water vapor adsorption studies on organomontmorillonites show that a smaller amount of water is taken up than by the original clay saturated with inorganic cations,[309-311] and the specific surface area as measured by water vapor adsorption is reduced.[309-312] Montmorillonite with alkylammonium or pyridinium-type counterions has only one or two layers of water between the unit layers in aqueous suspension, compared to four, and greater than 30, for the analogous calcium- and sodium-substituted clays, respectively.[312-314] The decreased affinity for water is attributed to a lesser degree of hydration of organic counterions (as compared to inorganic cations), and to blocking of the clay surface by bulky, hydrophobic organic groups.[312] This is further supported by the fact that the hydrophobicity of an organoclay increases with increasing size of the organic counterion.[307,310]

Organomontmorillonites exhibit a much greater affinity for organic solvents than do montmorillonites saturated with inorganic cations: sodium montmorillonite does not swell at all in liquid benzene, whereas analogous organoclays take up one to two interlayers of benzene. A pyridinium montmorillonite was found to adsorb five times as much benzene vapor as the sodium clay from which it was made.[309] Alkylammonium montmorillonites swell in most organic solvents[63,307,313] and may be readily dispersed in these liquids.[315] Pure alcohols do not appear to cause swelling of, or even interact strongly with, organomontmorillonite,[246,313,316] although when present in small amounts in nonpolar organic solvents they may be selectively adsorbed and cause an increase in floc volume;[316] the latter effects are limited to alcohols with three carbon atoms or less.

The effects of organic anions on clays are considerably less dramatic. Only negative adsorption of anionic 2,4-D (*p*-dichlorophenoxyacetic acid) by montmorillonite and kaolinite, was reported.[180] On the other hand, long-chain fatty acids (as sodium salts) seem to slightly adsorb on montmorillonite and kaolinite, presumably by anion exchange at the edges of the particles.[272] Sodium salts of mono- and dibasic organic acids have a similar effect on the stability of kaolinite sols as sodium chloride or sodium nitrate (ref 36, 118, 147, 194, 300, 317), indicating little effect of the organic anion.

The clay surface catalyzes numerous organic reactions. Clay minerals are extensively used as petroleum cracking catalysts.[318-324] They are most effective when largely in their hydrogen form, either from acid treatment[320,321] or from treatment with ammonium followed by heating to remove ammonia.[324] Cracking temperatures are in the range of 400-500°.

The polymerization of styrene is catalyzed by acid-treated kaolin and other clays, but not by the corresponding sodium substituted clays.[325-327] It is believed that the reaction is initiated by proton donation from the Brønsted acid sites of the clay to the styrene molecule, followed by cationic propagation. Other work showed that Na, K, and Ba montmorillonites are inactive with respect to styrene polymerization, whereas Cu, Zn, Cd, Al, In, and Co montmorillonites are quite active.[328]

Other polymerization reactions may be enhanced by clays. Acid-treated clays catalyze the polymerization of dienes.[329,330] The polymerization of fatty acids without simultaneous decarboxylation occurs at montmorillonite surfaces that have been pretreated with acid[331] or acetic anhydride.[332] Kaolinite treated with phosphoric or sulfuric acid catalyzes the polycondensation of methyl ethers,[333] and acid clay is used as a catalyst for making the polychlorohydrins used in the production of epoxy resins.[334] The fact that montmorillonite can catalyze the condensation of amino acids and amino acid adenylates to give oligopeptides[335] suggests that clays may have contributed to the evolution of terrestrial life.

Dehydration of organic molecules can often be catalyzed by a clay surface. Catalytic dehydration of 1,4-butanediol at an acid clay surface yields tetrahydrofuran at temperatures below 350°;[336,337] at higher temperatures dehydration is more complete and some 1,3-butadiene is produced.[336] Alkyl, phenylalkyl, and acetylenic monoalcohols are dehydrated by acid-treated kaolin, montmorillonite, attapulgite, and other clays.[338-341] Clay minerals are also used as catalysts in some dehydration-condensation reactions, such as amination of *n*-hexyl[341] and cyclohexyl[342] alcohols, and the alkylation of benzene with ethanol.[343]

Addition of substituents to an aromatic ring is promoted by clay catalysts. Acid-treated clays catalyze alkylation of aromatic rings by alcohols, alkyl chlorides, and alkyl ethers.[343,344] Alkylation of aromatic systems by reaction with olefins is enhanced by acidified attapulgite,[345] kaolinite,[346] montmorillonite,[347,348] and Fuller's earth;[349] the last three clays also catalyze the monochlorination of biphenyl with chlorine gas.[350]

Catalysis by clay surfaces can lead to stereospecific reactions in aromatic systems. Ortho and para alkylphenols are isomerized by heating in the presence of acidified montmorillonite to give predominantly the meta-substituted isomers.[351-353] Acidic montmorillonite also catalyzes the alkylation of o-phenylphenol to give the product in which both the alkyl and the phenyl groups are meta to the hydroxyl group.[351] This preference for the meta position clearly shows the effect of the catalyst, as the hydroxyl group is strongly ortho,para directing. On the other hand, primarily ortho-substituted products were obtained when phenol was substituted with an olefin in the presence of clay and sulfuric acid;[349] ortho substitution was also favored in the clay-catalyzed addition of chlorine to biphenyl.[350] The para position is favored when *tert*-butyltoluene is formed from the reaction between toluene and isobutylene in the presence of a clay catalyst.[345]

A number of specific reduction reactions are promoted by clays. Montmorillonite catalytically reduces some organic acids to ketones[354] or hydrocarbons.[355,356] Montmorillonite and vermiculite reduce Fe(III) to Fe(II) in Prussian Brown,[357] and acid-treated clays enhance the reduction of sulfur dioxide by methane to give elemental sulfur.[358]

Other reactions that are catalyzed by clays include the decomposition of diazoacetate,[359] the high-temperature dehydrogenation of butane to give butylene,[360] the hydrogenation of epichlorohydrins to produce chlorohydrins,[361] and the incomplete oxidation of methane at elevated temperatures to yield formaldehyde.[362]

TABLE III. Critical Coagulation Concentrations (ccc) of Sodium and Calcium Ions for Various Samples of Kaolinite and Sodium Montmorillonite (pH ≃7)

	Swartzen-Allen and Matijević[118]	Hsi and Clifton[370]	Kahn[369]	Williams and Drover[14]
ccc[a] of Na^+ for kaolinite	1.6×10^{-2}	7×10^{-3} to 1.2×10^{-2}		5×10^{-3} to 10^{-2}
ccc of Na^+ for sodium montmorillonite	3.5×10^{-3}		2×10^{-3}	(4×10^{-3}; not a pure montmorillonite)
ccc of Ca^{2+} for kaolinite	2.5×10^{-4}	5×10^{-4} to 10^{-3}		
ccc of Ca^{2+} for sodium montmorillonite	1.3×10^{-4}		10^{-4} to 2×10^{-4}	

[a] All concentrations are expressed in molarities.

E. Polymers and Polyelectrolytes

Polymer interactions with clay sols are in many ways similar to those of smaller organic molecules. The additional characteristic is the polymer bridging of clay particles which has been suggested by a number of investigators.[100,129,363]

Uptake of positively charged polymers by ion exchange with clay counterions appears to follow a Langmuir-type isotherm.[2,129,364] Bentonite holds cationic polysulfone so strongly that it cannot be exchanged by sodium or calcium ions.[365] Clays often adsorb polycations beyond the cation exchange capacity, resulting in reversal of charge.[129,363]

Anionic polymers are adsorbed onto the edges of the clay platelets,[100,101,106] having the same effect on the edge-to-face association in a clay sol as raising the pH.[100] The Langmuir-type isotherms indicate that physical adsorption forces are important in addition to anion exchange.[106] It was also noted that adsorption of anionic polyacrylonitrile on kaolinite increases with increasing charge of the metal counterion present,[366] which led to the suggestion that multivalent cations contribute to interparticle polymer bridging.[367]

Nonionic polymers also adsorb on montmorillonite.[101,368] Depending on the amount taken up by the clay, such uncharged polymer may either inhibit interparticle association or cause flocculation via polymer bridging.[368]

III. Colloidal Stability of Clay Suspensions

Ideally, the stability of colloidal systems may be evaluated from double layer theory. Attractive and repulsive potentials are calculated as functions of the interparticle separation and then summed; the resultant potential is usually strongly positive (repulsion) at very low separations and may exhibit negative minima (attraction) and positive maxima at larger separations. Coagulation occurs when the particles can approach each other and remain at the distance where a minimum in the potential *vs.* separation curve occurs. For this to happen, any repulsive maxima at greater separations must be low enough to be overcome by the thermal energy of the particles, yet the attractive potential well must be deep enough to prevent the particles from separating because of Brownian motion.

Usually, coagulation is brought about by a reduction in the electrical repulsion of the like charged double layers around the particles. This can be accomplished if the diffuse part of the double layer is compressed by the addition of electrolyte; in this case, the charge of the counterions plays the dominant role. Furthermore, the adsorption of counterions into the Stern layer (*i.e.*, immediately adjacent to the particle surface) will reduce the particle charge, and consequently the repulsive potential.

In clay suspensions[368a] the situation is considerably more complicated than in dispersions of ideal sols. In acid and neutral media edge-to-face flocculation occurs because of the presence of negative basal faces and positive edges; double layer compression, resulting from the addition of electrolyte to the system, will reduce the edge-to-face attraction in addition to reducing face-to-face and edge-to-edge repulsion. Hence, small amounts of electrolyte may initially deflocculate the clay; eventually, higher electrolyte concentrations coagulate it. The mode of interparticle association in the coagulated clay will depend upon the conditions under which the sol was coagulated; permeability data[89] and electron micrographs[55,83,84] indicate that the structure of the aggregates formed depends on the pH and the nature and concentration of the coagulant.

As one would expect, various studies have shown that in the electrolytic flocculation of kaolinite, montmorillonite, and the synthetic hectorite-type clay Laponite, the concentration of the salt required for destabilization decreased with increasing charge on the cations (ref 14, 76, 118, 369–373); in general, kaolinite appears to be somewhat less sensitive than montmorillonite to the presence of simple salts. For cations of the same charge, the coagulating efficiency increases with increasing ion exchange preference of the clay for the cation.[76,118,371] Some typical coagulation concentrations are summarized in Table III.

In general, the amount of face-to-face aggregation of a montmorillonite sol increases and its colloidal stability decreases with increasing charge and unhydrated radius of its counterions (ref 55, 69, 70, 72, 73, 77, 78, 87, 92, 95, 97, 98, 138). In kaolinite, the counterion has little or no effect on the degree of face-to-face aggregation.[20,98] If the counterions are not hydrolyzed, the stability of montmorillonite and kaolinite generally increases with increasing pH,[118] reflecting the breakup of edge-to-face flocculation.

Studies on the effect of pH on coagulation of clays have usually involved hydrolyzable ions commonly used in water treatment.[124,133,374,375] In these cases, the effect of pH on the coagulant is more important than its effect on the clay itself. Indeed, it was found that the change in the critical coagulation concentration of aluminum nitrate as a function of pH for silver halide[376] and sodium montmorillonite sols[118] was very similar at pH >4, although these colloidal systems behaved quite differently in the presence of simple cations. Optimum pH for coagulation of clays by aluminum or ferric ions occurs at the values slightly below the point of zero charge of the corresponding metal hydroxides.[118,124,133,374]

The flocculation of montmorillonite by quaternary ammonium cations depends primarily on the amount of cation adsorbed on the surface of the particles.[377] It was established that the sols are destabilized by these counterions when about 15% of the available surface area is covered, regardless of the size of the cation. This degree of surface coverage is similar to that observed during the destabilization of montmorillonite by cobalt(III) chelate complexes.[118]

As mentioned before, anion adsorption on the edges of the particles can stabilize clay sols by breaking up the edge-to-face structure in the flocculated state. It has been shown that montmorillonite and kaolinite are deflocculated by the adsorption of hydroxide, phosphate, oxalate, sulfate, acetate, chloride, metasilicate, and other anions (ref 8, 13, 16, 20, 21, 23, 24, 38, 100, 102–104, 122). It was also observed that small amounts of montmorillonite may break up the structure in a flocculated kaolinite dispersion;[21] this was attributed to the adsorption of the negative montmorillonite particles onto the positive edges of the much larger kaolinite platelets.

Small, uncharged organic molecules by themselves have little effect on the stability of aqueous clay suspensions,[118,378] although they may sensitize the clay to coagulation by metal counterions.[378]

The effect of positively charged polymers on the colloidal stability of clays depends on the concentrations of polymer and clay in the system. For example, at very low concentrations of polymer, clay sols are stabilized by adsorption of cationic polyacrylamide.[364] This may be because the highly hydrated polymer binds additional water to the clay, thus rendering the particles more hydrophilic, or because the partial neutralization of negative face charge brings about a breakdown in the edge-to-face flocculation.

At higher concentrations of polycation, the clay sol is destabilized.[105,129,363] This is commonly explained to be due to polymer bridging and supported by data indicating that the coagulating efficiency of a positively charged polymer increases with increasing molecular weight.[379] Coagulation could also be caused by reduction of particle charge; indeed, optimum destabilization was observed at the point of zero charge.[105] Adsorption of polycations beyond the cec results in charge reversal and restabilization.[129,363]

The ability of low concentrations of negatively charged polymers to stabilize clay suspensions has been attributed to adsorption of the polyanions on the positive edges of the clay platelets, causing deflocculation.[100,101] Some authors[364] have found that, at high pH, negatively charged polymers did not further deflocculate their clay suspensions, probably because the edges of the particles had already been neutralized by hydroxide ion. In higher concentrations anionic polymers eventually flocculate clay sols;[363] again, polymer bridging has been suggested, although not necessarily proven.

The presence of moderate amounts of nonionic polymers generally stabilizes clay suspensions;[101,368] it has been suggested that the uncharged macromolecules adsorb onto the surface of the clay particles and act as highly hydrated buffers, inhibiting interparticle association.

Finally, the ability of adsorbed polymers to stabilize colloidal suspensions under some conditions has also been considered thermodynamically.[380] Two factors contribute to an increase in the energy of repulsion between two colloidal particles which have adsorbed significant amounts of polymer. At close approach the thermal motion of the free ends of the adsorbed macromolecules is hindered sterically, leading to a decrease in their entropy and a corresponding increase in repulsive forces between the particles. Also, the relatively high concentration of polymer molecules in the region between two approaching particles causes a high osmotic pressure differential between this interparticle region and the bulk solution; this favors the situation in which there is more solvent (and hence more distance) between the particles. These factors will help to determine the colloidal stability of a clay sol with adsorbed polymer molecules, especially in the case of nonionic polymers, where there are no charge effects.

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